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High-yield sputtering events for Ar^+-ion bombardment of Cu in the energy range 1–20 keV

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A comparison of sputtering statistics for high- and low-index crystal planes of Cu subjected to Ar^+-ion bombardment is presented and some high-yield events are analyzed in detail. It is shown that a significant contribution to the average sputtering yield at 20 keV comes from a small number of ion trajectories which sputter a large number of atoms and that the damage produced by such impacts can be spread laterally for distances of the order of a hundred Angstroms or more.

I. INTRODUCTION

Recent experiments[1,2] in the scanning tunnelling microscope (STM) have examined the impact of individual ions on atomically flat crystal surfaces. These experiments have shown that small craters form as a result of a single ion impact in the 20 keV energy range and upwards.

Studies of surface topographical growth after ion bombardment have shown that strange topographies can occur as a result of energetic ion bombardment on pure crystal surfaces with contaminant free ion beams. One of the most remarkable examples of surface topographical development[3] occurs on the (3 11 1) surface of Cu. [The convention here will be to use the second Miller index to refer to the normal direction to the surface and the coordinate directions (x,y,z) to be aligned with the major crystal axes]. In a series of experiments over a number of years, Whitton and co-workers have examined the formation of topography on this particular crystal plane for a number of pure metals subject to inert gas ion bombardment usually at normal incidence in the energy range 15–40 keV. The results of this work can be summarized as follows. Pyramids with distinct facets cover the crystal surface and these are micron sized after doses of the order of 10^{19} ions/cm^2. These features do not develop on this crystal face for ion energies much less than 20 keV. On the neighboring (0 1 0) crystal surface a few large etch pits were observed to develop, but no pyramids.

Topographies such as those observed can occur as a result of multiple atom ejection from single impacts. This paper is a preliminary study of this phenomenon which compares the changes in the sputtering mechanisms as the bombardment energy increases from 1 to 20 keV on the two crystal surface (0 1 0) and (3 11 1) of single crystal Cu. Molecular dynamics calculations carried out at lower energies showed initial evidence of pit formation on the (0 1 0) surface of Cu,[4] but no comparative study of the differing atom ejection mechanisms between high and low index crystal planes or of the effect of ion energy has been carried out.

Changes in surface morphology as a result of ion bombardment by energetic ions has important applications in the semiconductor industry where small scale patterns can be etched, either directly by finely focused beams, or using masks. Ion bombardment is also used in highly sensitive surface analytical techniques such as secondary ion mass spectrometry (SIMS) but here the effect of topographical growth is to distort depth profile measurements.

For pattern delineation on the scale of a few hundred angstroms, nonlinear wave or Monte Carlo models can be used to predict and explain the resulting surface shapes which occur.[5,6] However, these models predict that a flat contaminant free surface bombarded by a uniform beam would remain flat (or at least flat to statistical accuracy). The continuum models give accurate descriptions of the formation of pits and cones on impure surfaces but cannot explain the process on the atomic scale.

II. THE MODEL

The sputtering simulation program used in this work was based on the QDYN code.[7,8] The programs were run assuming pair potential interaction functions between particles of the Born-Mayer type. The Ar^+-Cu potential function used was Shulga's modification to the standard Moliere potential (modified Bohr radius $a_0 = 0.092$ Å). The Cu-Cu atom-atom potential was a "Copper-Gibson" potential with a Morse well, previously used in studies of inert gas ion bombardment of Cu. These potentials slightly overestimate the experimentally measured sputtering yields. Accurate angular distributions can be obtained by using many-body interaction potentials, such as the embedded atom method.[9] Electronic energy loss and thermal vibrations were not taken into account in the model and the cascade calculation terminates when the maximum kinetic energy of a particle left in the target had dropped to 2 eV. The target sizes chosen for most of the simulations consisted of 1626 atoms for the (0 1 0) surface, 8 lattice units (l.u. where 2 l.u.$=a_0$, the length of the fcc unit cell) deep and 18×18 l.u.^{2}. For the (3 11 1) surface the target size was 1616 atoms, 6.47 l.u. deep (38 layers) and 22×22 l.u.^{2}. These target sizes were found, *a postiori,* to be sufficiently large to contain laterally the collision cascades for most impacts. However, at higher energies some cascades formed in which a larger number of particles left the sides of the target. These will be discussed in more detail later but it should be noted that the calculations for these trajectories can considerably underestimate the sputtering yield and larger targets should be chosen for improved accuracy. The simulations were carried out at normal incidence and a set of 300 impact points over a small representative area near the center of the target was selected for analysis. This number was increased to 600 at 20 keV to improve the statistics. The area representative of the surface as a whole, over which the impact points were distributed, was the square bounding adjacent surface atoms for the (0 1 0) surface and the smallest parallelogram within which the lattice structure is repetitive for the (3 11 1) surface, see Fig. 1. The lattice structure is periodic with depth every 2 l.u. for the (0 1 0) plane but every 11.4 l.u. in the (3 11 1) orientation, i.e., considerably below the depth at which most of the sputtered particles originate.

Some larger targets were also analyzed for those trajectories which deposit most of their energy near the surface and which sputter large numbers of particles. The largest target analyzed for the (3 11 1) representation consisted of 11 795 atoms, 12.58 l.u. deep (76 layers) and 44×44 l.u. square in area. Even a target of this size proved to be of insufficient size to contain the lateral spread of one cascade at 20 keV. Thus damage from a single event can spread to distances across the surface of the order of hundreds of angstroms in extent.

III. RESULTS

The spot patterns (azimuthal sputtered atom distributions) are relatively unaffected by an increase in energy and are not shown here. The same is also true for the longitudinal angle distribution. The proportion of atoms emitted as a function of energy also did not show substantial change as a function of energy. The principal difference here was between the two crystal planes with a higher peak at lower energies for the (0 1 0) plane compared to the (3 11 1) plane. The longest ejection times of all the sputtered particles occurred for incidence on the (3 11 1) plane at 1 keV, but these times are still well below those characteristic of thermal processes, the longest time at which a particle was emitted being approximately 600 fs (1 fs$=10^{-15}$ s).

The significant difference between sputtering at 1 and 20 keV, evident from Fig. 2, occurs in the statistical distribution of the atoms emitted per single impact. At 1 keV the distribution of the number of atoms per single particle impact [calculated mean ≈ 4.1 for the (3 11 1) plane, see Fig. 2(a)] has a statistical distribution whereby a large proportion of the yield comes from impacts which sputter around the mean number of atoms. The mode and the mean of the distribution are approximately the same. Only one trajectory at 1 keV, emitted more than 20 atoms. At 20 keV, however, the mode of the distribution of the number of emitted atoms per impact point is now at zero, where 83 of 300 impact points produced no sputtered atoms; see Fig. 2(c). In addition, a small number of trajectories produced very large yields. If the total contribution to the overall yield is examined (Fig. 3), a significant amount comes from a small number of impact points which produce high yields. The same trend is also seen for the (0 1 0) face, but of the 300 trajectories run at 20 keV, 200 produced no yield due to channeling and so the statistics is less good. The statistical distribution of the sputtering yield as a function of impact position at 20 keV has now changed to one in which the overall yield is critically dependent on the small number of trajectories which produce a large contribution. At an intermediate energy of 5 keV, events which produce similar high yields begin to appear. Of the 300 impact points examined, 53 produced no yield and five produced yields of 30 atoms or more; see Fig. 2(b). The corresponding trend is evident for bombardment on the (0 1 0) face [Figs. 2(d) and 2(e)] although here channeling is evident at 1 keV, where 17% of the incoming particles eject no atoms.

Although for a detailed statistical analysis many more impact points need to be considered to examine thoroughly the effects of those trajectories which produce high yields, it is clear that as the impacting ion energy increases in the energy range 1–20 keV, the total sputtering yield is derived from a decreasing number of impacts. As might be expected, for the (0 1 0) plane, the presence of wide open channels mean that a very high proportion of the ions (approximately $\frac{2}{3}$ at 20 keV) emit no atoms. These impact points are located in the channels between surface atoms and produce damage much deeper in the crystal. Sputtering only occurs for impact points close to surface atoms.

It is interesting to compare the differences in the collision between ions of 1 keV and 20 keV on the (0 1 0) surface with particular reference to a focused collision sequence which can occur if the ion is incident in the (1 0 0) or (0 0 1) plane. This is a somewhat artificial choice since in the absence of thermal vibrations, all the momentum imparted to the target will be confined to a plane in the initial part of the cascade. If a target atom is hit by the incoming ion in a head-on collision, the ion is reflected and a focused collision sequence propagates deep into the

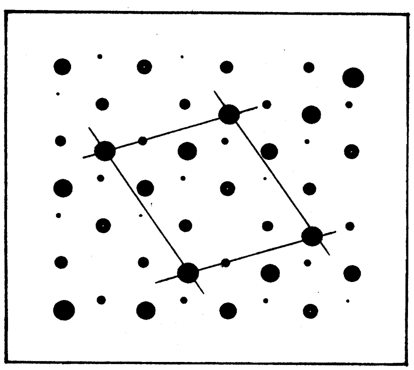


FIG. 1. A plan view of the (3 11 1) surface of Cu. Atom positions are shown as circles whose radii diminish with depth. Only the top ten layers are shown here. The smallest area on which impacts can occur which is representative of the whole crystal surface is a parallelogram. One such parallelogram is highlighted. The set of impact points was distributed over this area. For the (0 1 0) surface the representative area chosen was the square bounding adjacent surface atom positions.

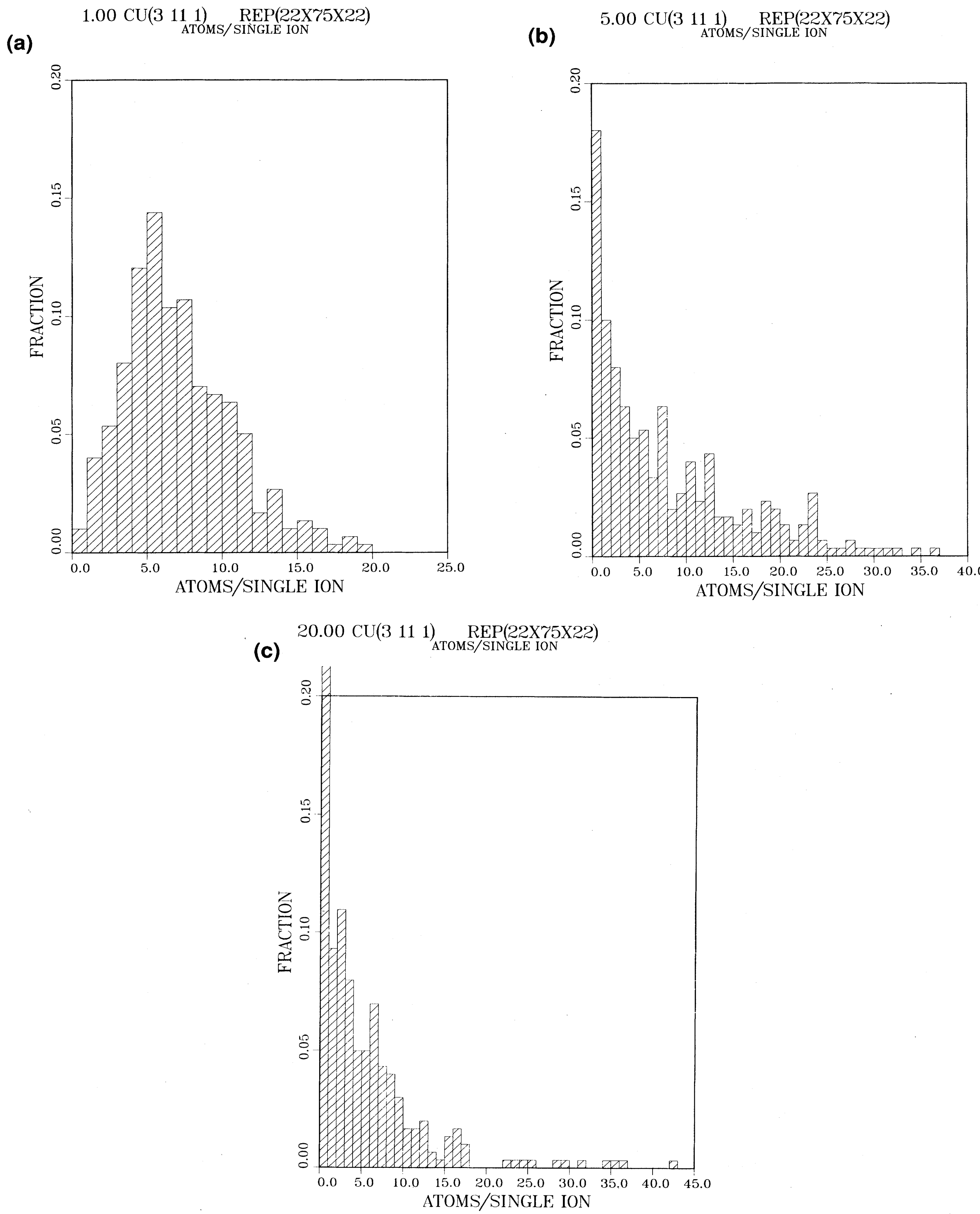
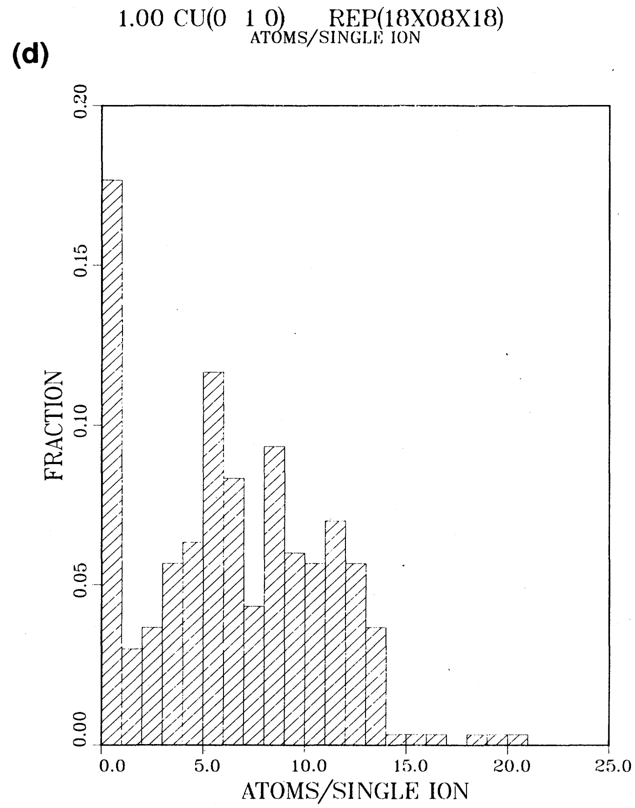


FIG. 2. Plots showing the atoms per single ion distribution for the (3 11 1) surface (a) 1.0 keV, (b) 5.0 KeV, (c) 20.0 keV and the (0 1 0) surface (d) 1.0 keV and (e) 20.0 keV. Each plot consists of 300 impact points.



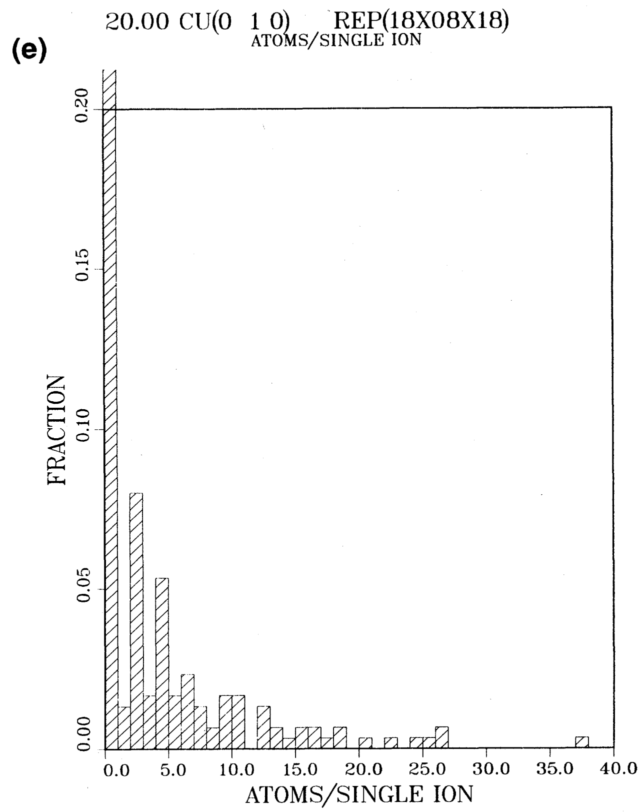


FIG. 2. (*Continued*).

crystal and causes no sputtering. However it is possible to choose an impact point in this plane close to a head-on collision which again pushes the primary recoil deep into the crystal but where the subsequent collisions of this recoil impart sufficient lateral momentum to produce ejection. This choice can be optimized to produce a high-sputtering yield. For an impact point displaced 0.01 l.u. in the x direction from a head-on collision, on a target 18×18 in area and 8 l.u. deep, 26 particles were ejected with 15 leaving the sides of the crystal. The effect of displacing the atoms causes forces in the target in the z direction but these remained small throughout the duration of the cascade. All emitted particles had their initial positions in the (1 0 0) plane. The target was then increased in size along the direction of the cascade to $34\times 20\times 8$ to determine the effect of particles which left the sides. The yield increased to 42 atoms, again all the emitted atoms coming from along the (1 0 0) plane. The yield for this target was enhanced due to edge effects because the crystal was of insufficient size to contain the cascade laterally with 15 particles leaving the sides. A sequence of shots in the development of this cascade are shown in Fig. 4. Finally the target size was increased to $50\times 20\times 8$. Now only four atoms left the sides of the target and only one of these within 1 l.u. of the surface. The cascade had been almost totally contained laterally and the sputtering yield was reduced to 32 atoms. The emitted atoms were seperated laterally by a maximum distance of 28 l.u. for this trajectory. The 32 were made up of thirteen from the surface, eight from the second layer, six from the third, two from the fourth, and one from the fifth, sixth, and eigth.

In order to compare the effect of ion energy on a trajectory such as this, it was reduced to 1 keV and the impact point again chosen in the (1 0 0) plane. The impact point was varied along the x direction until the sputtering yield was a maximum. In this case a target size of $20\times 8\times 34$ proved sufficiently large to contain the cascade. Only six atoms were ejected, five from the surface layer and only one from the second layer. The ejected atoms were emit-

TABLE I. Percentages of atoms ejecting from each atomic layer. Data from the (3 11 1) plane. The layer spacing is 0.175 l.u. (=0.316 Å).

layer	1	2	3	4	5	6	7	8	9	10	11	12	13	>13
20 keV	18.9	18.2	15.8	16.7	11.6	8.1	4.3	1.8	0.8	1.3	1.3	0.6	0.5	1.0
1 keV	18.3	19.2	13.9	16.7	10.6	10.4	4.5	1.6	1.5	1.3	0.7	0.5	0.3	0.3

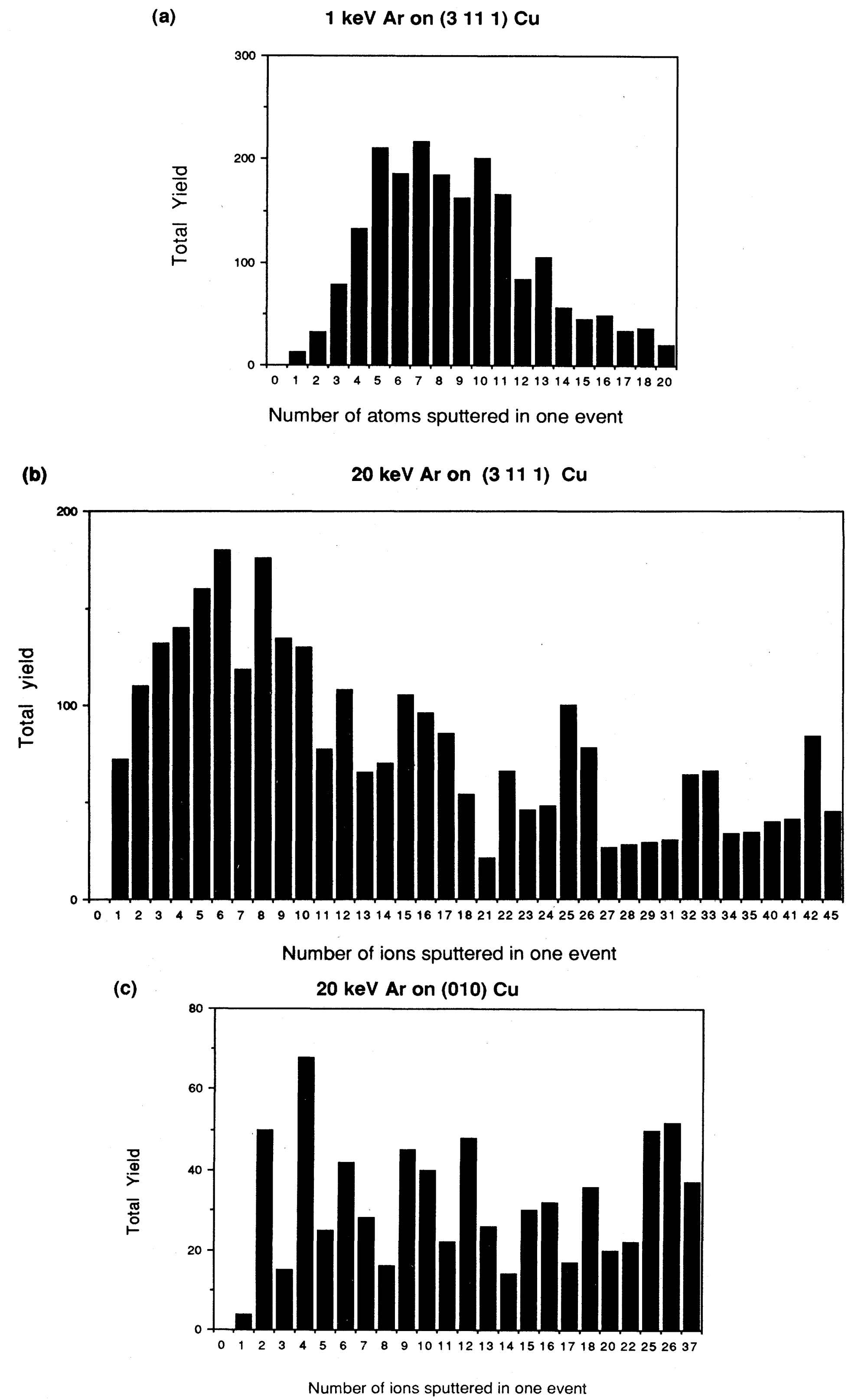


FIG. 3. Plots which show the total sputtering yield as a function of the number of atoms emitted in a single event for the (3 11 1) surface at (a) 1 keV and (b) 20 keV. The 20-keV data set contains 600 impact points, double the number for the 1-keV data set. (c) The corresponding figure for the (0 1 0) surface at 20 keV for a set of 300 impact points.

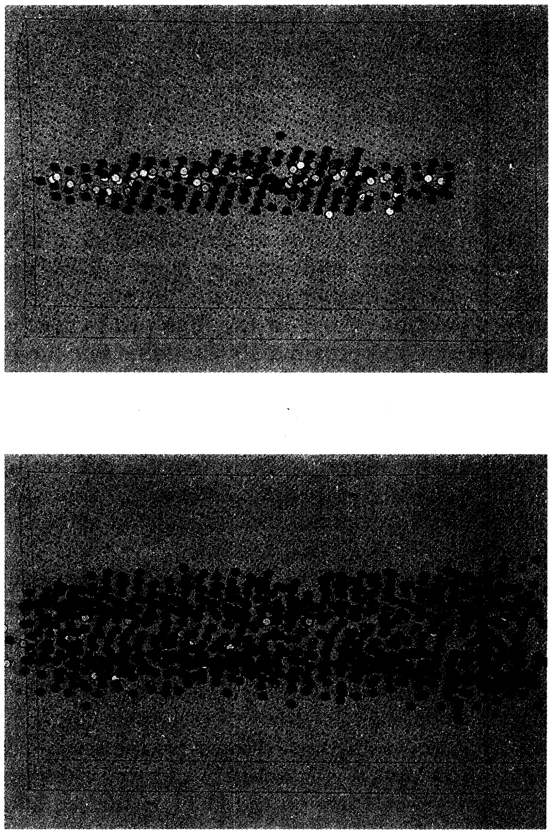


FIG. 4. Two snapshots viewed at 16° off normal incidence and depicting a focused collision sequence from a 20-keV Ar^+ ion at normal incidence on the (0 1 0) face of single crystal Cu. The particles are colored to represent their energy according to the scheme given below. The striped particle is the incident ion. Only particles which come within the sphere of influence of a moving particle are colored. The centers of undisturbed particles are colored as black dots. The time sequence is (upper) 40 fs; (lower) 174 fs. The incident ion is reflected and after 4 fs leaves the target, but imparts > 18 keV of kinetic energy to the primary recoil which eventually leaves the bottom of the target but imparts lateral momentum to neighboring atoms which causes the large spread of the cascade. The color simulations were carried out on a MacIntosh II (Ref. 10), which uses the RGB color scheme whereby colors are assigned co-ordinates in three-dimensional red, green, blue space with co-ordinates from 0 to $2^{16}-1$. Thus black is (0,0,0), white is $(2^{16}-1,2^{16}-1,2^{16}-1)$, red is $(2^{16}-1,0,0)$, etc. For particles within the target, undisturbed atoms are shown as black points; low-energy particles are colored red$\rightarrow$yellow$\rightarrow$white for high energy on a logarithmic scale according to

$$\frac{\ln(1+\mathrm{KE})}{\ln(2000)} .$$

Here the kinetic energy (KE) of a particle is in electron volts and any particle whose kinetic energy is greater than 1999 eV is colored white. Particles which lie above the initial surface are colored from dark blue$\rightarrow$cyan$\rightarrow$white with the same logarithmic scaling. Note that not all particles colored blue are sputtered. They must still have enough energy to escape from the attractive part of the interaction potential.

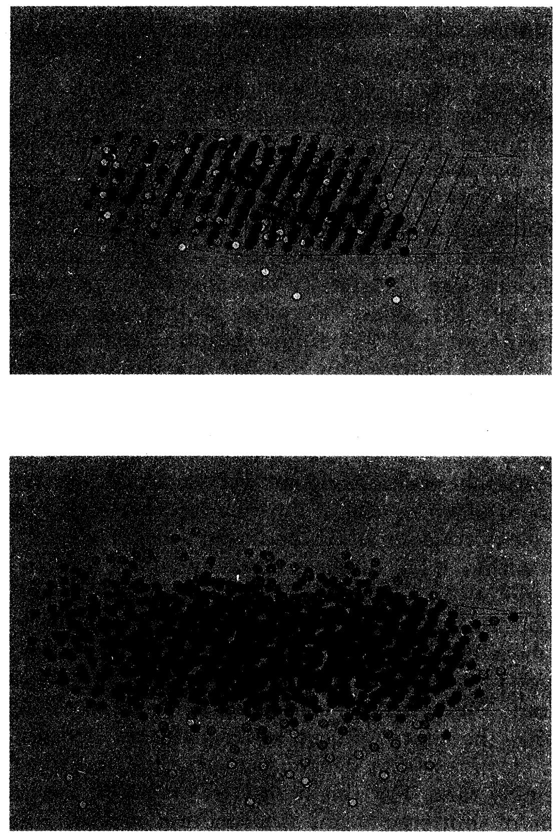


FIG. 5. Two snapshots showing the development of a cascade following bombardment of a 20-keV Ar^+ ion at normal incidence on the (3 11 1) face of single crystal Cu. The particles are colored using the same color scheme as in Fig. 4. The viewing angle is now 86° from normal. The time sequence is (upper) 49 fs; (lower) 232 fs. Most of the sputtering has taken place by $t=345$ fs, at which time over 70 atoms have been ejected from the surface, 44 particles have left the bottom surface of the target, and 31 from the sides. For color scheme see Fig. 4.

ted from points which were 4, 6, and 8 l.u. distant from the impact point on one side and 10 and 12 l.u. on the other. A change in energy from 1 to 20 keV not only increases the yield substantially for this type of trajectory but also increases the lateral spread and deepens the depth of origin of the sputtered particles, despite a reduction in the calculated sputtering yield for the surface as a whole.

The above trajectory contained a number of symmetries which might be important in the development of morphological features, since removal of atoms in a given preferred direction is how such features may begin to form. For impacts, at normal incidence, on the (3 11 1) plane, no semiplanar trajectories such as this occur. A more typical asymmetric trajectory, which also produced a large sputtering yield, was therefore chosen for detailed analysis. In this case the incoming ion undergoes a series of hard collisions close to the surface and the primary knockons themselves remain close to the surface long enough to cause considerable damage. The impact point was chosen to be one which produced a high sputtering yield. For this trajectory, the original target size chosen was far too small to contain the cascade; the crystal literally was "blown to pieces" by the impact. Two stages in this process are shown in Fig. 5. A much larger target was therefore chosen which consisted of 11 795 atoms 44×44 l.u. square and 12.58 l.u. deep. After all the sputtered atoms had been ejected 9751 atoms within the target had been set in motion. This target also was of insufficient size to laterally contain the cascade and 46 atoms left the sides. Because of this, the calculated sputtering yield of 134 atoms should only be seen as an approximate figure. This number was one of the highest recorded for a single impact and some ejection times were longer than in the more typical cascades but no ejections occurred after 750 fs. The sputtered atoms were ejected from original positions which were separated laterally by distances of up to 40 l.u. but in contrast to the previous high-yield trajectory, 71% of the ejected atoms came from within 1 l.u. of the surface and 18% within 2 l.u. No atom ejected originated at a lattice site deeper than 2.8 l.u. (18 layers on this surface). This trajectory took four days to calculate on a MacIntosh II and so a detailed analysis of only a few high-yield trajectories has been carried out. Nevertheless, the information seems to suggest, as with the more typical lower-yield trajectories, that atom ejections from deeper than the first few layers are extremely rare. For this high-yield trajectory, the distribution of sputtered atoms as a function of depth followed the same statistical trend as that for the mean of all trajectories with 86% of all ejected atoms coming from the first seven atomic layers (equivalent to 1.05 l.u. in depth). Analysis for other high-yield events showed the same trend with the exception of the one focused collision sequence for the (0 1 0) plane mentioned earlier. The depth of emission of sputtered particles does not appear to be energy dependent or depend on the surface crystal plane. The uniformity of the depth of origin of the sputtered particles is shown within the tables. It should be pointed out that the 2% of sputtered particles emanating from below the third atomic layer for the 20-keV bombardment of the (0 1 0) plane came almost entirely from focused collision sequences such as described above and depicted in Fig. 4.

TABLE II. Percentages of atoms ejecting from each atomic layer. Data from the (0 1 0) plane. The layer spacing is 1 l.u. (=1.807 Å).

Layer	1	2	3	>3
20 keV	86	10	2	2
1 keV	90	9	1	0.4

The results have indicated the diverse nature of the sputtering event and its critical dependence on initial ion energy, crystal face, and impact point. This critical dependence can be further illustrated by slightly varying the impact position of one of the high-yield trajectories. The yields remain approximately the same but the particles which are emitted can show large differences. This is the definition of a chaotic event where small changes in initial conditions can cause large changes in the system. High-yield events appear to be inherently chaotic in nature. This is hardly surprising since a collision cascade propagates like a tree and a small change in an early part of the cascade affects all that follows.

With the exception of the focused sputtering sequence mentioned above, the study of single events has revealed little correlation between sputtered atoms. Such correlations would be necessary to explain symmetric morphological development on sputtered surfaces. Work is now in progress to determine if such correlations can occur as a result of multiple impacts. However, the initial results appear to show that this is unlikely and that the peculiar topographies which form on the (3 11 1) surface of some metals may well arise due to the implantation of Ar within the target structure after large doses, rather than from inherent crystallographic effects of the (3 11 1) surface.

It has not been possible to quantify the extent of the lateral spread of surface damage from this study because this would require a detailed study of the final state of all the cascades that have been run. What can be said is that because sputtered atoms always originate close to the surface, there is a direct correlation between the high-yield events and the lateral spread of the cascades near the surface.

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†Deceased 8/24/88.

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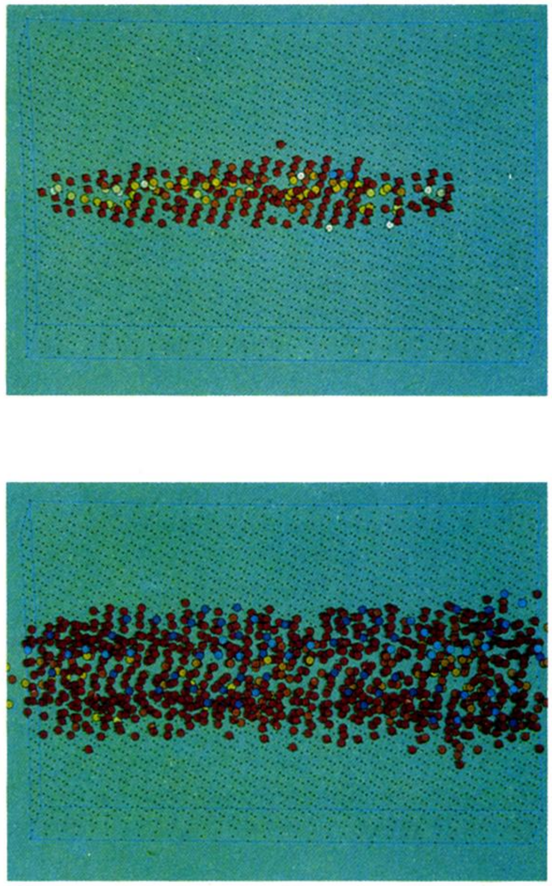

FIG. 4. Two snapshots viewed at 16° off normal incidence and depicting a focused collision sequence from a 20-keV Ar^+ ion at normal incidence on the (0 1 0) face of single crystal Cu. The particles are colored to represent their energy according to the scheme given below. The striped particle is the incident ion. Only particles which come within the sphere of influence of a moving particle are colored. The centers of undisturbed particles are colored as black dots. The time sequence is (upper) 40 fs; (lower) 174 fs. The incident ion is reflected and after 4 fs leaves the target, but imparts >18 keV of kinetic energy to the primary recoil which eventually leaves the bottom of the target but imparts lateral momentum to neighboring atoms which causes the large spread of the cascade. The color simulations were carried out on a MacIntosh II (Ref. 10), which uses the RGB color scheme whereby colors are assigned co-ordinates in three-dimensional red, green, blue space with co-ordinates from 0 to $2^{16}-1$. Thus black is (0,0,0), white is $(2^{16}-1, 2^{16}-1, 2^{16}-1)$, red is $(2^{16}-1, 0, 0)$, etc. For particles within the target, undisturbed atoms are shown as black points; low-energy particles are colored red$\rightarrow$yellow$\rightarrow$white for high energy on a logarithmic scale according to

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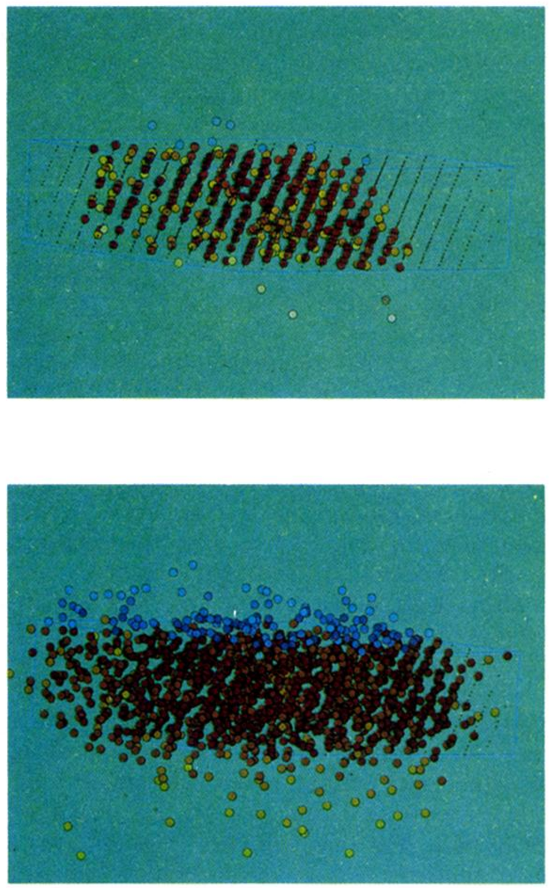

FIG. 5. Two snapshots showing the development of a cascade following bombardment of a 20-keV Ar^+ ion at normal incidence on the (3 11 1) face of single crystal Cu. The particles are colored using the same color scheme as in Fig. 4. The viewing angle is now 86° from normal. The time sequence is (upper) 49 fs; (lower) 232 fs. Most of the sputtering has taken place by $t = 345$ fs, at which time over 70 atoms have been ejected from the surface, 44 particles have left the bottom surface of the target, and 31 from the sides. For color scheme see Fig. 4.